EFFECTS OF HYDROSTATIC PRESSURE ON THE MECHANICAL BEHAVIOR OF BODY CENTERED CUBIC REFRACTORY METALS AND ALLOYS

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ABSTRACT

The influence of the volume proportion of second-phase particles on the decrease in flow stress for a series of annealed iron-carbon alloys after subjection to a hydrostatic pressure of 20 kilobars has established that the maximum change occurs for alloys containing 1 to 2 vol.% for the particular morphology used. The existence of an increase in the minimum or critical pressure for the development of pressure-induced changes in yield behavior with increase in volume of second phase is indicated. Examination of microyield characteristics has demonstrated that the introduction of mobile dislocations by pressurisation results in a substantial decrease in the microyield stress σ_A compared with the values obtained by the normal method of uniaxial plastic prestraining at atmospheric pressure.

Measurements of tensile ductile-brittle transition behavior for fully recrystallised commercial purity tungsten and tungsten-1 wt.% thoria alloy after subjection to a hydrostatic pressure of 20 kilobars show no change in transition temperature, within the accuracy of measurement, from that of the as-recrystallised materials. A rapid method of preparing thin foils for transmission electron microscopy from the 0.030 in. diameter wire tensile specimens has been developed and used to establish the nature of the substructural changes on annealing the as-received drawn wires at successively higher temperatures. The tungsten foils contained very few impurity second phase particles, but large numbers of sub-micron sized internal voids were observed for the recrystallised condition. Dislocations do not develop from the voids on pressurisation. Foils from the alloy showed that the thoria was present in a range of shapes, and sizes ranging up to approximately 1 micron. The volume fraction of thoria is greater than that corresponding to the nominal composition of 1.9 vol.%. The thin foil observations are shown to be in keeping with the nature of the pressure response of the mechanical behavior of these materials and the dislocation generation hypothesis.

I. INTRODUCTION

During the 12-month period of the present research program (beginning 1 June, 1965), the principal objectives have been to: (a) study pressure effects on iron and iron-carbon alloys as being a model system for the investigation of the mechanism of dislocation generation under hydrostatic pressure and of the variables controlling the magnitude and nature of the effect; and (b) continue the study of the effect of pressure on ductile-brittle behavior by investigating the influence of substructure and second-phase particles in tungsten and tungsten-thoria alloys. The investigation now involves a second graduate assistant, Mr. P. Trester who joined the research program in September 1965, in addition to Mr. G. Das who joined the program in 1964. Mr. Das has continued with the research on tungsten and tungsten-thoria alloys and Mr. Trester is studying the model system. In addition, H. Ll. D. Pugh (Head of the Plasticity Division, National Engineering Laboratory, U.K.) who is the holder of the Republic Steel Corporation Distinguished Visiting Professorship at Case for the academic year 1965-66, is participating during this period in several of the research activities in the High Pressure Laboratory, including some aspects of this current study of pressure effects on structure and mechanical behavior of bcc metals.

The present report describes the research carried out during the six-month period beginning 1 December 1965. During this period, the research effort has been directed to clarifying the effects of pressure cycling up to 25 kilobars on ductile-brittle transition behavior in tungsten and tungsten-1% thoria alloys, with

particular attention to microstructure aspects. In addition, measurements of pressure effects on the discontinuous yield phenomena in high purity iron-carbon alloys and a commercial plain-carbon steel (AISI-1018) have been continued as part of the study of quantitative relationships between pressure, dislocation structure and changes in yield characteristics. Some effects of pressurisation on microyield phenomena have been investigated.

II. IRON-CARBON ALLOYS

In the case of this model system of second-phase particles dispersed in a matrix of isotropic linear compressibility, suitable methods for specimen preparation and observation of yield behavior in tension were established previously[1] for large specimens (0.15 in. gage diameter x 1 in.gage length) from which thin foil specimens can be prepared directly. Tests on annealed specimens of an Fe-0.65 wt.%C alloy after subjection to a hydrostatic pressure of 20 kilobars showed the expected successive lowering of the stress for yielding and the elimination of the upper yield point[2,3] and confirmed the selection of this particular model system. The current work has been concerned with establishing accurately the magnitude of the decrease in yield stress for a constant applied pressure as a function of the volume proportion of the second phase (Fe_3C) and the change in yield stress as a function of applied pressure for a given volume proportion; with developing a suitable method for producing controlled dispersion of spheroidal carbide particles; and with investigating the influence of pressure on the micro-yield region of the stress-strain curve. The methods of specimen preparation and vacuum annealing, pressurising and

tensile stress-strain measurement in the axial loading rig were as described previously[1] except for some modifications in the methods of strain measurement which are discussed below. All tests were conducted at room temperature. Strain rates of 0.05 and 0.02 $in.min^{-1}$ were used for the macroyield and microyield tests, respectively. The pressurised specimens were tested as soon as possible after subjection to pressure; in the case of unavoidable delays, the specimens were stored at $0^{o}C$ or below to prevent possible "strain-aging" effects.

(a) Macroyield Phenomena

In the previous report[1], some preliminary observations were presented of the changes with pressure in the form of the macroyield region of the tensile stress-strain curve, as measured from both the load-cell output and cross-head movement on the Instron constant strain-rate machine. These observations have now been extended using a new type of extensometer (see later in this section) for the 0.065 wt.%C (1.0 vol.% Fe_3C) alloy and the 0.18 wt.%C (2.8 vol.% Fe_3C) steel, in order to investigate the magnitude of the changes in yield stress as a function of the applied pressure. The grain diameters for these two materials after annealing were 0.04 mm and 0.016 mm, respectively. The results of the investigation are shown in Figure 1 plotted in terms of the reduced or normalised change in yield stress (i.e., the difference between the 0.2% offset yield stress after pressurising and that in the initial as-annealed condition divided by the initial yield stress). It is seen that for the 0.18 wt.%C steel that there is a 'critical' pressure in the vicinity of 15 kilobars below which no change in the yield stress is apparent and above which the yield stress

decreases continuously with increasing pressure. In a previous investigation of the initial stages of the pressure effects in a 0.03 wt.% (0.5 vol.% Fe_3C) alloy[3], such a 'critical' pressure for the lower yield stress occurred at a much lower value in the region of 4 to 5 kilobars. This is shown in Figure 1, by data taken from stress-strain curves in this reference. Although in the present work, tests have not been made for such low pressures, the results shown in Figure 1 for the 0.065 wt.%C alloy do suggest a critical pressure of this magnitude. It is not yet known whether the higher critical pressure required for the 0.18 wt.%C steel is attributable to the particular dispersion and greater amount of second phase or to effects of solute impurities on the strength of the matrix. In either case, the present results indicate a possible reason for some of the variability in the pressure response of steels observed in several different laboratories. It is especially interesting to note that once its critical pressure is exceeded, the response of the steel rapidly reaches that of the lower carbon alloy. This suggests that the amount and morphology of the carbide are the important factors.

The influence of the volume proportion of second phase on macroyielding was investigated by conducting tensile tests on the following series of high purity iron-carbon alloys - 0.004, 0.02, 0.065, 0.30 and 0.55 wt.%C, corresponding to 0.06, 0.35, 1.0, 4.7, and 8.6 vol.% Fe_3C - before and after subjection to hydrostatic pressure. In addition, similar tests were conducted on the 0.18 wt.%C (2.8 vol.% Fe_3C) plain carbon steel (AISI-1018). All the compositions

were pressurised to 20 kilobars except for the 0.55 wt.%C alloy, which was subjected to only 18 kilobars due to the occurrence of a leak in the high pressure apparatus during that particular run. In place of the method of strain measurement used earlier[1] for the measurement of tensile strain, a new type of extensometer - the Instron Extensometer - of 1 in. gage length was attached to the specimen. The extensometer incorporates a small beam on an amplification arm and fitted with resistance strain gages; the beam bends elastically during the elongation of the specimen and the strain gage output measures the corresponding strain in the specimen. This method was found to be almost as sensitive in the microstrain experiments as directly mounted gages, and has the advantages of being simpler in use and of averaging the specimen strain in the lower yield stress region when the inhomogeneous Luders extension is taking place. A minimum of 4 tensile specimens - two pressurised and two as-annealed - were used for each composition.

The resulting changes in yield stress as a function of the volume proportion of Fe_3C are shown in Figure 2. The change is plotted in terms of the decrease in 0.2% offset yield stress from the values for the unpressurised specimens. Some earlier results on a series of plain-carbon steels containing more than 0.2 wt.%C and in the normalised condition[2] are also included in Figure 2. The general form of the present results in the same composition region is in good agreement - in particular as to the gradual disappearance of the pressure-induced changes in yield stress with increasing volume proportion of carbide. The differences

in the magnitude of the changes for the two sets of results are attributable to differences in experimental materials, conditions and techniques. It is to be noted that, despite these, the earlier data agree closely with the present results for the similar type of plain-carbon steel, AISI-1018.

The results for the alloys with a lower volume proportion of Fe_3C establish clearly the existence of a maximum effect of pressure between 1 and 2 vol.% Fe_3C. The rapid increase in the effect with increasing second phase content at levels below this is in accordance with the hypothesis of pressure-induced generation of dislocations which predicts an increase in the number of mobile dislocations and therefore a greater decrease in yield stress as the proportion of hard particles increases[2]. The magnitude of the effect in the 0.004 wt.%C alloy (a 'high purity' iron, Ferrovac E) is larger than might be expected, but it is possible that some impurity particles are also contributing to the effect in this material. These have been observed in thin-foils. The maximum and the subsequent diminution of the effect shown in Figure 2 with further increase in the second phase content is considered to be associated with the increasing mutual interference of the pressure-induced strain-fields at adjacent particles. The point at which the maximum occurs, and its value, should also depend on the morphology and distribution of the particles.

For the present annealed structures in the higher carbon alloys, it is known from thin-foil electron microscopy studies earlier in the program that the carbide occurs principally as

partly spheroidised clusters in which a high dislocation density persists even after prolonged annealing. This structure would be expected to inhibit the pressure-induced generation of mobile dislocations to a much greater extent than for a uniform dispersion of particles. Accordingly, as part of the investigation of the influence of the morphology of the second-phase distribution, a subsidiary study was undertaken to establish a suitable technique for developing a uniform dispersion of spheroidal carbide particles in these iron-carbon alloys. This aspect of the program was carried out as an undergraduate research problem by Mr. N. J. Dimitris and Mr. R. F. Duncan in collaboration with Mr. Trester. As it was also known from earlier work that the method of thermal cycling about the eutectoid temperature ($720^{o}C$) to facilitate uniform nucleation was unsatisfactory for these alloys, the study was directed to the methods of spheroidisation by prolonged annealing of normalised alloys at temperatures just below that of the eutectoid ('sub-critical annealing'), and by the tempering of martensitic structures in the region from 430^{o}-$700^{o}C$. The effects of the time and temperature of these spheroidising processes on the microstructure were examined in detail for the 0.065 wt.%C alloy using light microscopy, carbon replica electron microscopy and lineal analysis techniques. The results show that the most uniform dispersion of near-spheroidal particles was obtained by the tempering method. Tempering at $700^{o}C$ for times of the order of 1 hour gave a suitable dispersion, with an average grain size of 0.015 mm. Less uniform dispersions of larger particles

and a larger ferrite grain size (0.054 mm) developed at prolonged tempering times of up to 10 hours. The density and distribution of dislocations in the tempered structures are to be examined by thin-foil electron microscopy.

(b) Microyield Phenomena

The stress-strain curves as measured initially from the Instron load-cell and the cross-head movement were found to deviate from the linear "elastic" relationship at stress values which decreased with increase in the pressure to which the specimens had been subjected. Accordingly, a procedure for making sensitive strain measurement was developed to examine this feature more precisely and to study its relationship to the pressure-induced generation of mobile dislocations. The injection of mobile dislocations and/or sources into the iron matrix without grossly changing the overall dislocation substructure, as can be accomplished by pressurising, offers an unusual opportunity to test out some of the implications of the dislocation dynamics analyses of yielding[5] and the importance of the role of interstitial solute-locking. In particular, it should make feasible a more direct study of the factors contributing to the stress required to move a dislocation in ferrite than has been possible previously.

The initial investigation of microyield phenomena in pressurised material has been carried out on annealed specimens of the 0.18 wt.%C steel after subjection to a pressure of 20 kilobars. Electrical resistance strain gage measurement of microstrain was adopted as the method of following the early stages of plastic flow.

Two foil strain gages (Micro Measurements Inc., Type No.EA-06-031DE-120) were placed 180^{o} apart on each specimen so that the linear strain could be recorded directly versus the output from a load-cell on a Mosley X-Y recorder during the tensile tests. For comparison, stress/strain was recorded independently and simultaneously by standard Instron measuring procedures.

Two methods - continuous and cyclic loading - were used to detect the initial permanent strain developed. In the first method, the stress value for the initial deviation from the linear relationship during continuous loading (i.e., the limit of proportionality, σ_A) was measured. A typical result is shown in Figure 3, which compares the recorded load/strain data for an annealed specimen of the steel and one pressurised to 20 kilobars. The value of σ_A for the former corresponds closely with the upper yield stress of some 43×10^3 psi, the load for which is too high for inclusion in the graph. In contrast, the value of σ_A for the pressurised specimen is only 15.5×10^3 psi. In the second method, which has been developed considerably by N. Brown and co-workers in recent years[6,7], the specimen is repeatedly loaded and unloaded to successively higher loads. The stress at which the load/strain cycle first shows hysteresis defines the elastic limit σ_E (i.e., the stress for the initial movement of dislocations) and the stress for which the hysteresis loop no longer closes on unloading defines the microyield stress σ_A (the limit of anelasticity). The measured magnitudes of both of these parameters vary with strain sensitivity. For comparison purposes

in the present work, σ_A has been defined as the stress to give 10^{-5} in/in permanent strain on unloading. A typical series of load-unload stress-strain curves is shown in Figure 4 for a specimen of the same steel pressurised to 20 kilobars. Both the continuous and cyclic loading methods were found to give similar values for σ_A. A corresponding agreement between σ_A values from the two methods has been observed previously for a polycrystalline iron in which discontinuous yielding was eliminated by tensile pre-straining into or beyond the lower yield stress region[6].

Plastic pre-straining has been used widely to eliminate discontinuous yielding in studies of the early stages of plastic flow in iron. However, a major question concerning this technique is the extent to which the change in dislocation density and distribution resulting from plastic pre-strain affects the magnitudes of σ_E and σ_A . Kossowsky and Brown[7] in a recent investigation on polycrystalline zone-refined iron (12 to 15 ppm carbon) have shown that σ_A increases very little with increase in pre-strain from 0.001% to 0.2%, but increases rapidly with further increase in pre-strain up to the limit examined of 5%. In Fig. 5, a comparison is presented for specimens of the 0.18 wt.%C steel of the effects of tensile pre-strain and pressurising on the values obtained for σ_A as measured by the cyclic loading method. The results show that whereas a tensile pre-strain of 0.53% reduces $_A$ from some 43×10^3 psi in the annealed ('locked') condition to 25.4×10^3 psi, pressurising an identical specimen to 20 kilobars reduces σ_A to the substantially lower value of 15.5×10^3 psi.

Even after subsequently pre-straining this specimen in tension to 0.68% strain, σ_A is still slightly lower (23.2×10^3 psi) than for the first pre-strained specimen.

The value of the microyield stress at room temperature obtained after pressurising for this commercial purity steel of relatively high carbon content (0.18 wt.%) and small grain size (0.016 mm) is close to the σ_A value of 15×10^3 psi at room temperature reported for a Battelle zone-refined iron (0.001 wt.%C) and less than that of some 18×10^3 psi for a high purity iron (0.011 wt.%C)[6]. The grain size for both these irons was much larger, "about 0.1 mm" and the sensitivity of strain measurement greater than that used here. Unfortunately, Brown and Ekval[6] do not specify the actual pre-strain used in their measurements, but the later work[7] on apparently the same Battelle zone-refined iron reports σ_A values of only 6×10^3 psi for 0.1% pre-strain, increasing to some 13×10^3 psi for 5% pre-strain. Even with these uncertainties, it is clear that the values of σ_A achieved in an impure iron matrix by pressurising are comparable to those obtained in much purer iron of coarser grain size using the tensile pre-strain technique. Thus, the uniform and localised introduction of mobile dislocations into the iron lattice by pressurising[8] does have significant advantage for the study of initial dislocation movement. Pressurising experiments are currently in progress on the high purity iron and lower carbon alloys to examine the early stages of plastic deformation in the purer ferrite matrix.

III. TUNGSTEN AND TUNGSTEN-THORIA ALLOYS

Measurements were reported previously[1] concerning the influence of hydrostatic pressures up to 25 kilobars on the terminal ductile-brittle transition temperature, T_d, for electropolished tensile specimens prepared from powder metallurgy tungsten wire (0.030 in. diam.) of commercial purity as a reference material in the study of the role of second-phase particles in the response of brittle materials to pressurising. For specimens (Material W-3) annealed in vacuum at 1310°C and 1600°C, it was found that the transition temperatures (80°C and 190°C respectively) are unaffected, within the accuracy of measuring T_d, by pressure cycling. In contrast, earlier results for specimens from ostensibly the same batch of material annealed at a higher temperature to a coarser grained structure, showed a depression in T_d of the order of 50°C after pressurising to only 13 kilobars[9] together with associated changes in the form of the stress-strain curves. Analogous observations for a powder-metallurgy tungsten 1wt% thoria alloy vacuum annealed at 2000°C and 2200°C showed no measurable change in T_d (130°C and 180°C, respectively) on pressure cycling. The optical microstructures indicated that, even at 2200°C, the fiber structure is not completely removed in these alloys.

The current work has been directed to investigating the influence of the annealing condition on the response of tungsten W-3 and the tungsten-thoria alloy to pressure cycling - with respect to both mechanical behavior and substructure - with the objective of clarifying the roles of variations in impurity particle content and the perfection of substructure in determining the magnitude of the response.

(a) Mechanical Behavior

In order to obtain a microstructure of recrystallised grains of low density of dislocations in both the tungsten and the 1 wt.% thoria alloy i.e., an 'optimum' matrix for inducing the pressure response in the presence of second phase particles, a series of annealing experiments were carried out. Wire specimens were vacuum annealed for 30 minutes in tungsten crucibles at temperatures of 1800°, 2000°, 2200°, 2400° and 2600°C for the tungsten and 2400° and 2600°C for the thoria alloy. The resulting changes in grain width - measured optically on longitudinal cross-sections - are shown in Figure 6. For the tungsten, the grains remained elongated up to the higher temperature investigated - although the length to width ratio diminished substantially. It can be seen from Figure 6 that the grain width stabilises in the region of 2400°C. As the annealing temperature of 2200°C was found to reproduce most closely the microstructure of the earlier tungsten specimens[9], this temperature was selected for further pressurising experiments. The grain shapes in the thoria alloy also did not become completely equiaxed, but the 2600°C anneal (which was the highest temperature attainable with available vacuum furnace equipment) showed the most completely recrystallised structure and was accordingly chosen as optimum. (See Figure 6).

Batches of tungsten and thoria alloy specimens were annealed at these temperatures, subjected to a hydrostatic pressure of 20 kilobars and the tensile characteristics at atmospheric pressure determined for test temperatures up to 240°C. The methods of specimen preparation, annealing, electroshaping, pressurising in a modified piston-cylinder apparatus and tensile testing were similar to those

used and described previously[1]. The strain rate in the tensile tests was 0.025 $min.^{-1}$.

The results of the tensile tests for the tungsten annealed at 2200°C are shown in Figure 7 in the form of yield stress, fracture stress and reduction in area versus test temperature. As can be seen, the results for both the as annealed and the pressurised specimens plot on essentially the same curves, i.e., there is no change in transition temperature within the experimental error of measurement. Furthermore, the transition temperature is similar to that observed previously for specimens annealed at 1600°C. The transition temperatures observed in this material annealed at different temperatures are plotted in Figure 8 as a function of the logarithm of the optical grain size. The broad band on this graph denotes the approximately linear variation obtained[10] for a compilation of published data for tungsten. The data points for the 1310° and 1600°C annealing temperatures in the present work are seen to be in agreement with this Petch type relation. However, the point for 2200°C annealed tungsten lies above the band, corresponding to a lower transition temperature than predicted from the relationship.

The analogous results of the tensile tests for the 1 wt.% thoria alloy annealed at 2600°C are shown in Figure 9. As for the tungsten, the data for both the as-annealed and the pressurised specimens do not indicate a change in the transition temperature within the error of measurement. The actual value of T_d is slightly higher (~ 190°C) than for the previous highest annealing temperature of 2200°C (T_d ~ 180°C).

For tungsten, a response to pressurising had been expected if sufficient impurity particles were present in the particular material

used and sufficient pressure could be applied to induce dislocation-generation by differential compression of the particle and recrystallised matrix. The fact that essentially no changes in stress-strain response were observed except for the initial series of specimens suggested that in general the material contained too few suitable particles, but that variations in impurity content might be present. For the 1 wt% (1.9 vol.%) thoria alloy in the recrystallised condition, the apparent absence of changes in mechanical behavior was more surprising, in view of the maximum in the yield suppression observed in the Fe/Fe_3C alloys containing a similar volume proportion of second-phase particles - see Figure 2. In this case, it appeared that the applied pressure was too low in relation to the differential compression of the W and ThO_2, and the flow stress of the matrix - leading to no or insufficient generation of mobile dislocations. In addition, the morphology and distribution of thoria particles could be an important factor, as was found for the Fe/Fe_3C (see, for example, Figure 1). In an attempt to resolve these factors, an examination of the tungsten and the tungsten-thoria alloy by thin-foil electron microscopy was undertaken as described in the following section.

(b) Thin-Foil Electron Microscopy

The preparation of thin-foils suitable for electron transmission from 0.030 in. diameter tungsten wire specimens of the type used in the study of tensile behavior is normally both difficult and tedious. Stickler and Engle[11], and Meieran and Thomas[12] have recently described techniques of preparation using the jet dimpling method. In the present work, the jet method has been used with a number of

modifications in technique to facilitate the handling and thinning processes. The improved technique, which has also proved suitable for thinning 0.030 in. diameter wires of the 2-phase tungsten-thoria alloy, is described below prior to the discussion of the structural observations on the wires.

The preparation technique involves three principal steps: grinding the wire to a flat, electro-machining dimples with a pressurized microjet and, finally, bath electropolishing to foil. In the first step, a one-inch length of the 0.030 in. diameter specimen is embedded in a thin layer of a self-curing and cold setting resin ('Quick-Mount'). Conventional metallurgical mounting materials requiring curing at pressure and temperature are unsuitable because of the brittleness of annealed tungsten. The embedded specimen is ground by hand on fine polishing papers to a parallel sided flat approximately 0.010 in. thick. After removing the remaining resin and cleaning, 1/8" long sections are cut from the long specimen by spark machining. This method of cutting prevents the deformation and fracture of the specimen which occurs in using mechanical cutting methods. The 1/8 in. sections are of convenient size to mount directly in the electron microscope specimen holder.

In the second step, the production of dimples on opposite sides of the 1/8 in. section, the principal modification made is the use of a pressurized jet instead of a gravity-feed to give a controlled steady supply of electrolyte. The electrolyte (2% NaOH in water) is pressurized in a stainless steel vessel using compressed air at 20 psi. The pressure is controlled by the use of a pressure regulator (of a type

used in the welding of plastics) installed in between the electrolyte and the main air line (80 psi). A hypodermic needle of stainless steel, which also acts as cathode, is used as the nozzle of the jet. A small circular bore needle (#27, 0.017" o.d.) gave suitable dimpling but poor surface polish, while use of a larger bore jet (e.g. #25, 0.22" o.d.) gave a brilliant polish but too wide a dimple so that the edge support was lost. These difficulties were overcome by using a flattened hypodermic needle of 22 gage (.029" o.d.) which produces a suitably shaped dimple of bright polish by allowing sufficient electrolyte to flow through the nozzle to keep the specimen cool and thus avoid etching. The specimen is positioned under the jet by clamping in a self-locking stainless steel tweezer mounted on a stage which can be translated in two perpendicular directions in a plane normal to the jet. The specimen is first adjusted so that the jet strikes the center line, and then is translated back and forth along the longitudinal axis during dimpling to ensure a large electron transparent area after final bath polishing. Jetting is carried out for 90 seconds on each side at 120 volts D.C. with a current density of approximately 40 amp. cm^{-2} through the cathode and a specimen to needle-tip distance of 2mm. The first dimple is lacquered to prevent etching during dimpling on the other side of the specimen.

In the final step, electropolishing to foil is carried out in 2% NaOH solution with an applied voltage of 8 volts (from a D.C.battery supply) across the specimen and a stainless steel cathode, using an anode current density of 0.2 amp.cm^{-2}. The progress of the polishing is followed by observing the specimen against a light beam by means of low-power microscope arrangement. When a small hole appears, electropolishing is stopped and the specimen removed and washed successively

in hot water, acetone, ethyl alcohol and ether. This elaborate cleaning is found to be necessary to ensure a clean surface free from contamination such as can result from the "layer" formed during electropolishing.

Foils prepared in the above manner from the tungsten and tungsten - 1wt.% thoria wires were examined in a JEM 6A electron microscope operated at 100KV, using a 400 micron condenser aperture and a useful beam current of 100μA. Selected area diffraction was used to determine orientation relationships in the foils. The results of the examination are presented in the following sections.

For tungsten, the successive changes in substructure with increase in annealing temperature are illustrated in Figures 10a through 10f. (The micrographs are oriented so that the wire axes are approximately parallel in each set - along the page length in Figures 10 a,b,c, and diagonally in Figures 10 d,e,f). The as-drawn wire (Figs. 10a and 12a) consists of highly elongated grains or 'fibers' whose long axis is closely parallel to the wire axis of $\langle 110 \rangle$. The fiber width averages some 0.5 microns. Dense dislocation arrays and a cell structure are frequently observed within the fibers. After annealing at 700^{o}C (Fig.10b), widening of the fibers is apparent, together with occasional evidence of a more developed cell structure. At 1000^{o}C (Figs. 10c and 12b), transverse boundaries appear which segment the fiber and give a 'bulbous' type of widening fiber structure. The enlargement of fiber segments continues at 1300^{o}C (Fig. 10d) and by 1600^{o}C (Fig. 10e), the width between boundaries reaches the order of 5 microns. These general features of the structural changes on annealing are in good agreement with those reported by Meieran and Thomas[12] for temperatures up to 1500^{o}C. The fiber widths observed here are slightly larger, although the increase in width

with temperature is similar - see Figure 6. At the highest annealing temperature examined, 2200°C, a further increase in the distance between boundaries to as high as 20 microns occurs. The dislocation density within the grains is low and the dislocations mostly appear as hexagonal networks - Figure 12c. (It is interesting to note from Figure 6 that the spacing between boundaries observed by optical microscopy is consistently larger than that seen in the thin foils. However, an analogous relation to that for grain size (Figure 8) appears to hold between T_d and log. fiber width).

Extensive searches for impurity second phase particles were carried out at all stages of annealing of the powder metallurgy tungsten. Such particles were observed very rarely and always in grain boundaries - an example is shown in Figure 10f. In contrast with the few visible particles, a substructural feature which developed widely and increasingly with increasing annealing temperatures was the appearance of parallel rows of small circular features - see Figure 12c. From electron diffraction contrast experiments, these were identified as small voids within the foils. No such features are visible in the as-drawn wire (Figure 12a), or after annealing at 700°C. However, for 1000°C, strings of elongated voids are occasionally seen - mainly within enlarged fibers, as in Figure 12b. With further increase in annealing temperature, the voids appear in increasing numbers, varying sizes in the range 0.1 - 0.01 microns and more spherical in shape, In the recrystallised wire (1600°C and above) they are always spherical - Figures 10f, 12 - and the parallel rows of voids lie approximately parallel to the wire axis, $\langle 110 \rangle$, and are spaced some 0.5 microns apart.

Thus, they appear to correspond in position to the original fiber boundaries in the as-drawn wire. It has been pointed out[12] that the fiber boundaries in the wire correspond to the original grain boundaries prior to the application of working processes. If this is correct, then the voids observed here may be attributable to the presence of grain-boundary voids and/or dissolved gas, or grain boundary impurity compounds in the as-sintered material.

Features similar to the voids seen in the present study are visible - but unidentified as such - in several published electron micrographs of powder metallurgy tungsten, e.g. ref. 12. Recently, Wronski and Fourdeux[13] reported on a comparative thin foil study of powder metallurgy and melted tungsten. In 'as-received' commercial tungsten rod (0.2 in.diam. sintered and warm worked), the structure showed large elongated gas pockets, often associated with the fiber boundaries. After complete recrystallisation by annealing at 1730°C, spherical bubbles appeared in parallel rows, similar to those seen here. No such features were found in melted tungsten and its lower ductile-brittle transition temperature (by 100°C) was attributed to their absence.

The origin of the bubbles in either the Wronski and Fourdeux material or the present material is uncertain, but it seems likely that internal void formation may be a characteristic of partly or fully recrystallised sintered refractory metals i.e., attributable to the sintering process. In the presence of doping additions (as are often applied to minimise grain growth in the case of tungsten), voids could also arise from volatilisation on annealing of some of the compounds used. The wire used here was purchased as 'undoped', but its failure

to develop fully equiaxed grains on recrystallising suggests that some doping additions may be present.

For the tungsten-1 wt% thoria alloy, the structures seen in thin-foils from wires annealed at 2000° and 2200°C are illustrated in Figure 11. At the lower temperature, recrystallisation is incomplete and strong inhibition of grain boundary migration by thoria particles is frequently in evidence - as shown in Figure 11a. The thoria particles vary considerably in distribution, size and shape, the longest ones being 'rod' shaped and approximately 1 micron long by 0.5 micron wide. These rod particles tend to be aligned with their length parallel to the direction of the wire axis. Occasionally, the shape and spacing of adjacent particles indicated that they represented large original particles presumably fractured during the wire processing. At 2600°C, the matrix grains are larger and more equiaxed, with some indication of a less oriented array of rod particles i.e., of rearrangement of the particles. In contrast, in the only other reported thin foil study of thoriated tungsten[14], which was carried out on sintered and swaged rod of approximately 1/8 in. diameter, no evidence of rearrangement was observed for annealing temperatures up to 2700°C. The dislocation content of the tungsten matrix was low for both annealing temperatures. A characteristic of all the foils examined of the 1 wt.% ThO_2 alloy was that the volume proportion of thoria is greater than the expected 1.9 vol.%.

If the absence of effects of pressurising on the mechanical behavior of the tungsten and the 1 wt.% thoria alloy is in keeping with the hypothesis of pressure-induced generation of dislocations, the

substructure seen in thin-foils of the pressurised materials should show no, or severely limited, evidence of new dislocations. In the case of the tungsten, the only possible sources of elastic discontinuity (since second phase particles were almost completely absent in the foils examined to date) were the strings of small voids or gas bubbles present in the recrystallised material. In many instances, the voids in the as-recrystallised tungsten were associated with isolated dislocations or hexagonal networks impeding the movement of dislocations. From dislocation contrast experiments on the larger voids, a few examples were seen of loop segments close to the void-matrix interface; it appears likely that these may have formed as the result of local plastic strain to relieve the complex stresses associated with the void growth. However, despite the existence of the voids, acting as small elastic discontinuities, no evidence of additional pressure-induced dislocation was found in foils from the pressurised tungsten. Thus, the mechanical behavior and substructural characteristics are not in conflict. It has not yet been possible to prepare foils from the specimens used in the earlier experiments on W-3 tungsten which did show some pressure effects, but it anticipated that their examination will clarify this 'anomolous' behavior.

In case of foils prepared from the recrystallised and pressurized tungsten - 1 wt% thoria alloy, again no new dislocations were observed to have formed. The reason that dislocations could not be generated around these particles may be associated with the use of too small an applied pressure (20 kilobars) with respect to the relative linear compressibilities of the two phases. However, it is believed that the more likely cause is the presence of too large a volume proportion

of the thoria particles. As was shown for the model material earlier in this report, the intensity of the pressure response is a maximum in the vicinity of 1 to 2 vol.% second-phase and reduces rapidly with further increase in the volume proportion. The thin-foil examination discussed above showed that the volume proportion of thoria in the alloy used in the present investigation appears to be well above that corresponding to the suppliers quoted composition and,correspondingly, the desirable range.

It is of interest to note here that Schaffhauser, in a limited study of the effects of pressurising on the ductile-brittle transition temperature, T_d, in bend specimens of annealed commercial purity tungsten sheet and a tungsten -0.5% hafnium - 0.2% carbon alloy sheet, has recently reported decreases in T_d of 25^o and 50^oC, respectively, for pressurising to 15 kilobars[15]. In the case of the tungsten, thin-foils were examined in transmission and evidence was shown of dislocations generated from a precipitate particle at a grain boundary. Thin-foil examination was not carried out on the alloy, which showed the larger and more significant depression in T_d. However, both these results and those for chromium[16] do provide further support for the concepts under exploration in the current investigation.

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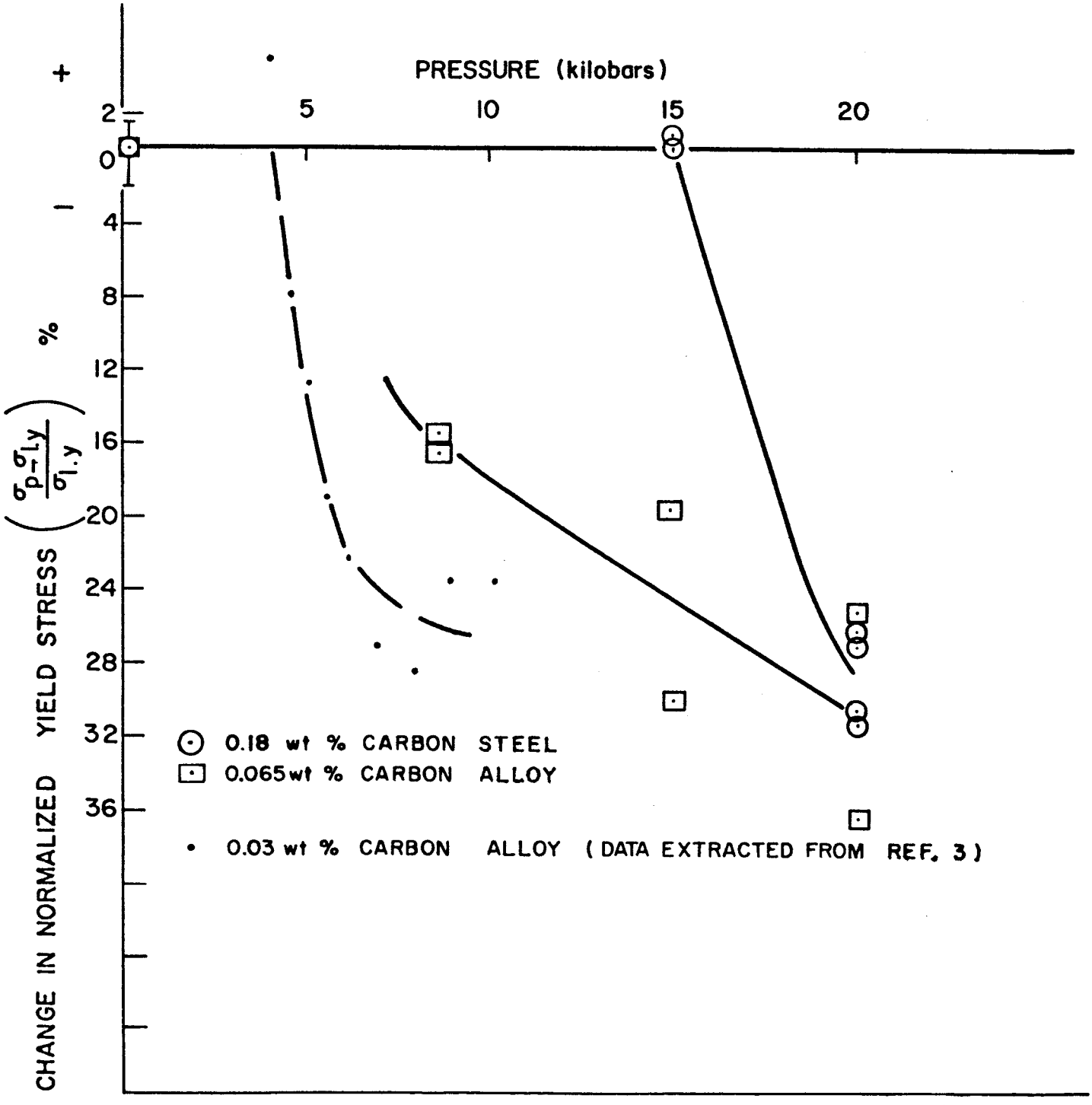


Fig. 1. Pressure dependence of the decrease in the normalised yield stress for 0.065 wt.%C alloy and 0.18%C steel.

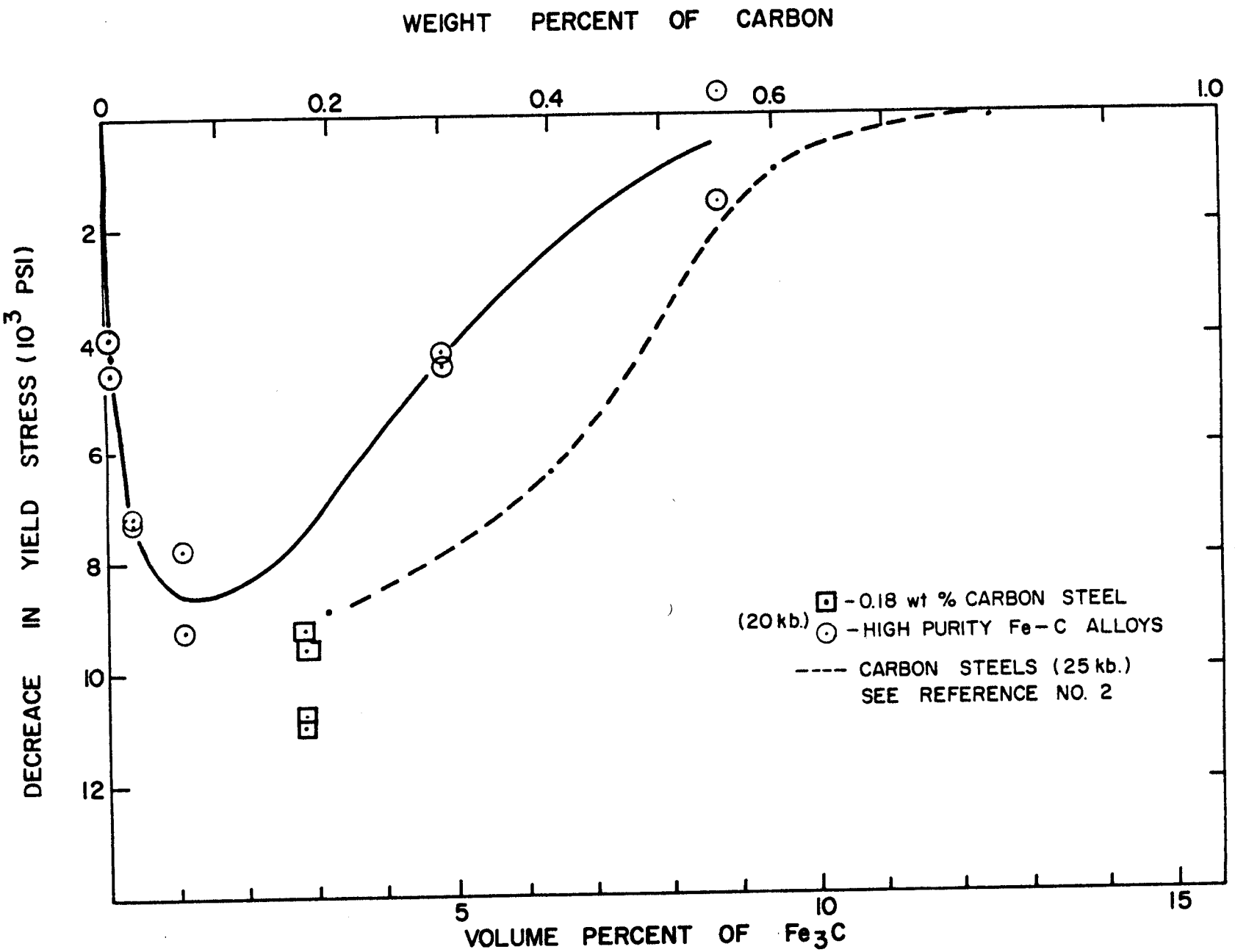


Fig. 2. Decrease in yield stress as a function of the amount of second phase (Fe_3C) in annealed iron-carbon alloys subjected to a pressure of 20 kilobars.

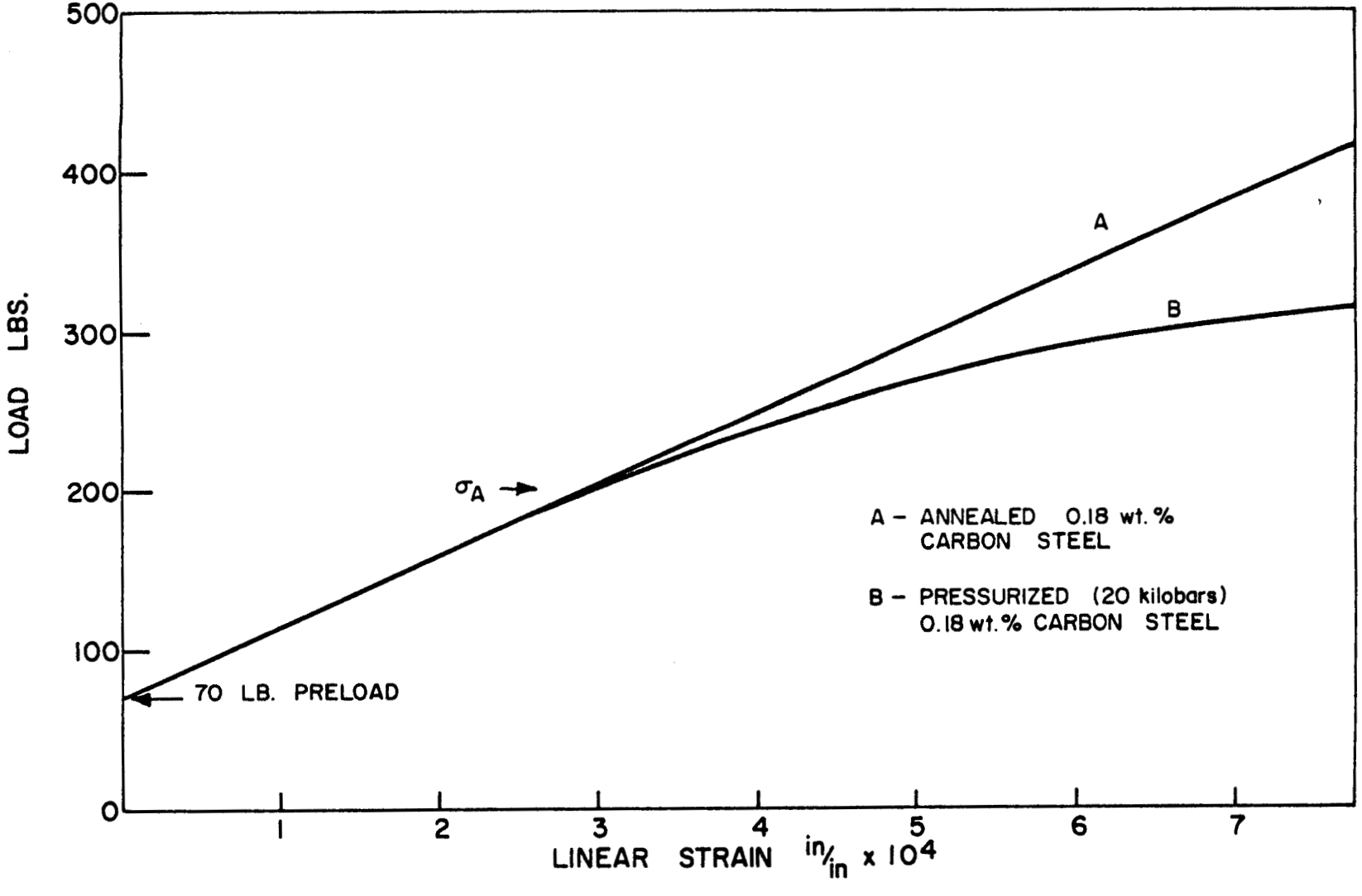


Fig. 3. Example of continuous loading method for determining σ_A of a 0.18 wt.% carbon steel subjected to 20 kilobars.

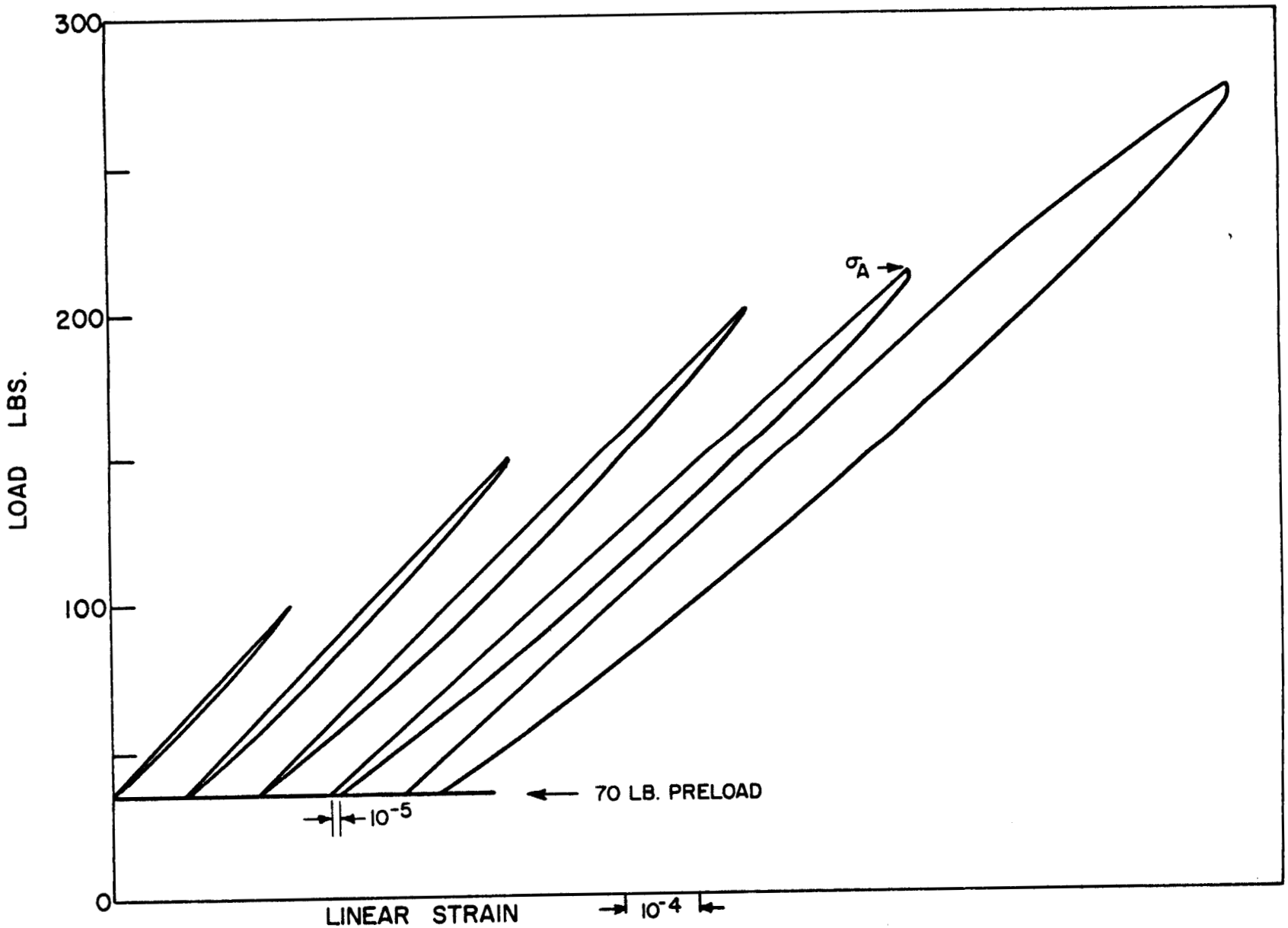


Fig. 4. Example of cyclic loading method for determining σ_A of a 0.18 wt.% carbon steel subjected to 20 kilobars.

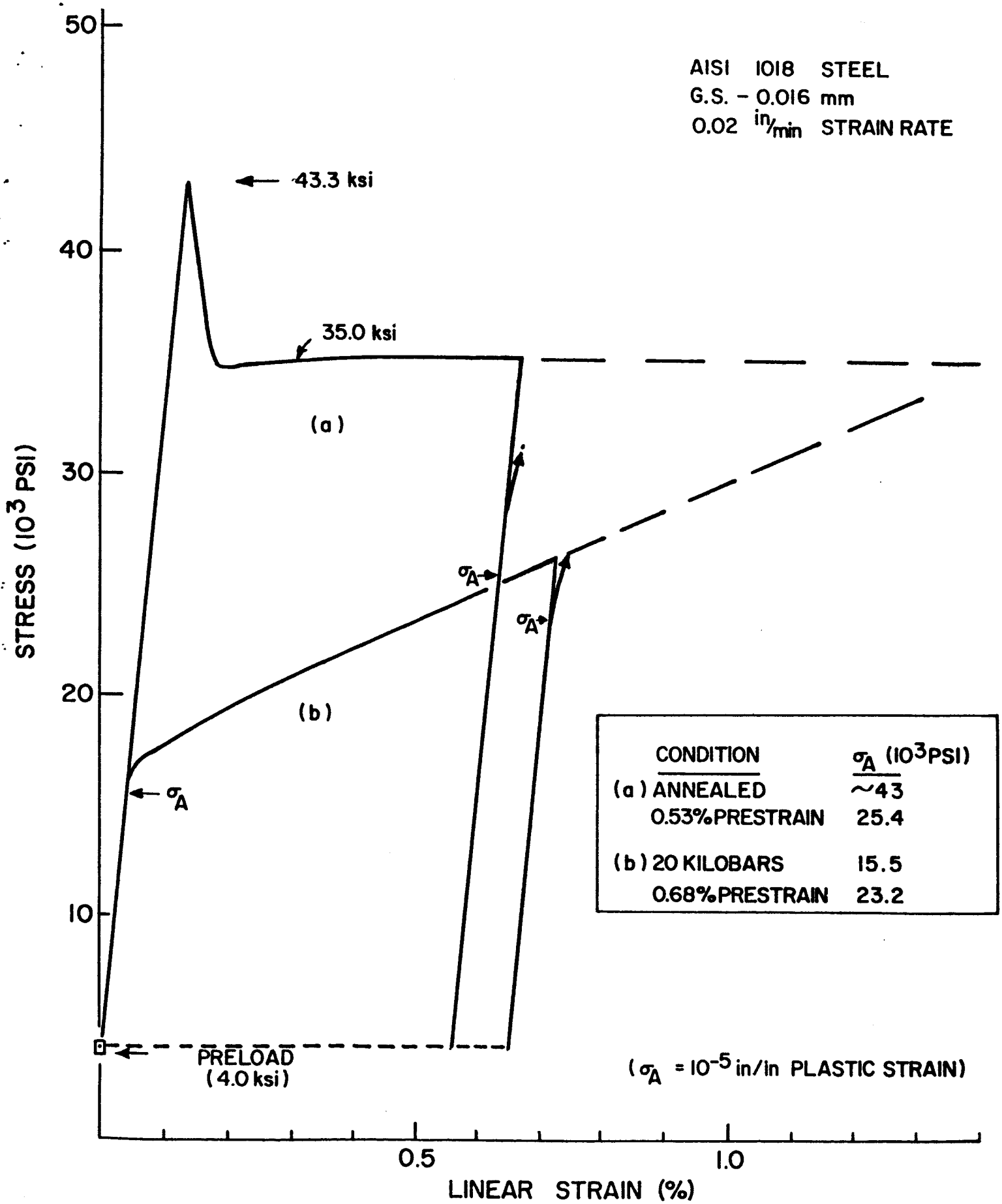


Fig. 5. Comparison of the effect of tensile prestrain and pressurisation on the magnitude of the initial flow stress σ_A.

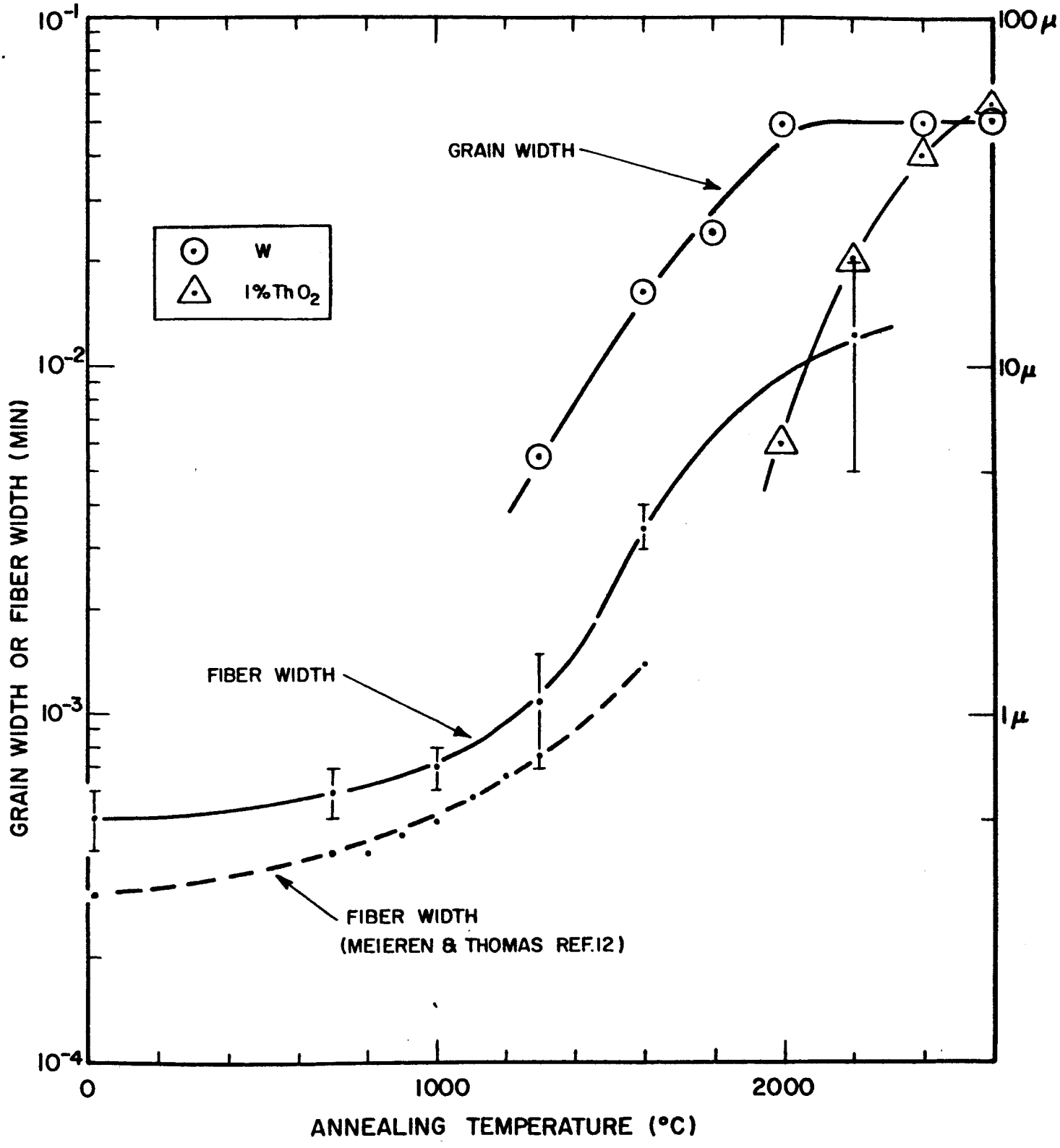


Fig. 6. Grain size and fiber width developed in powder metallurgy tungsten wire as a function of annealing temperature.

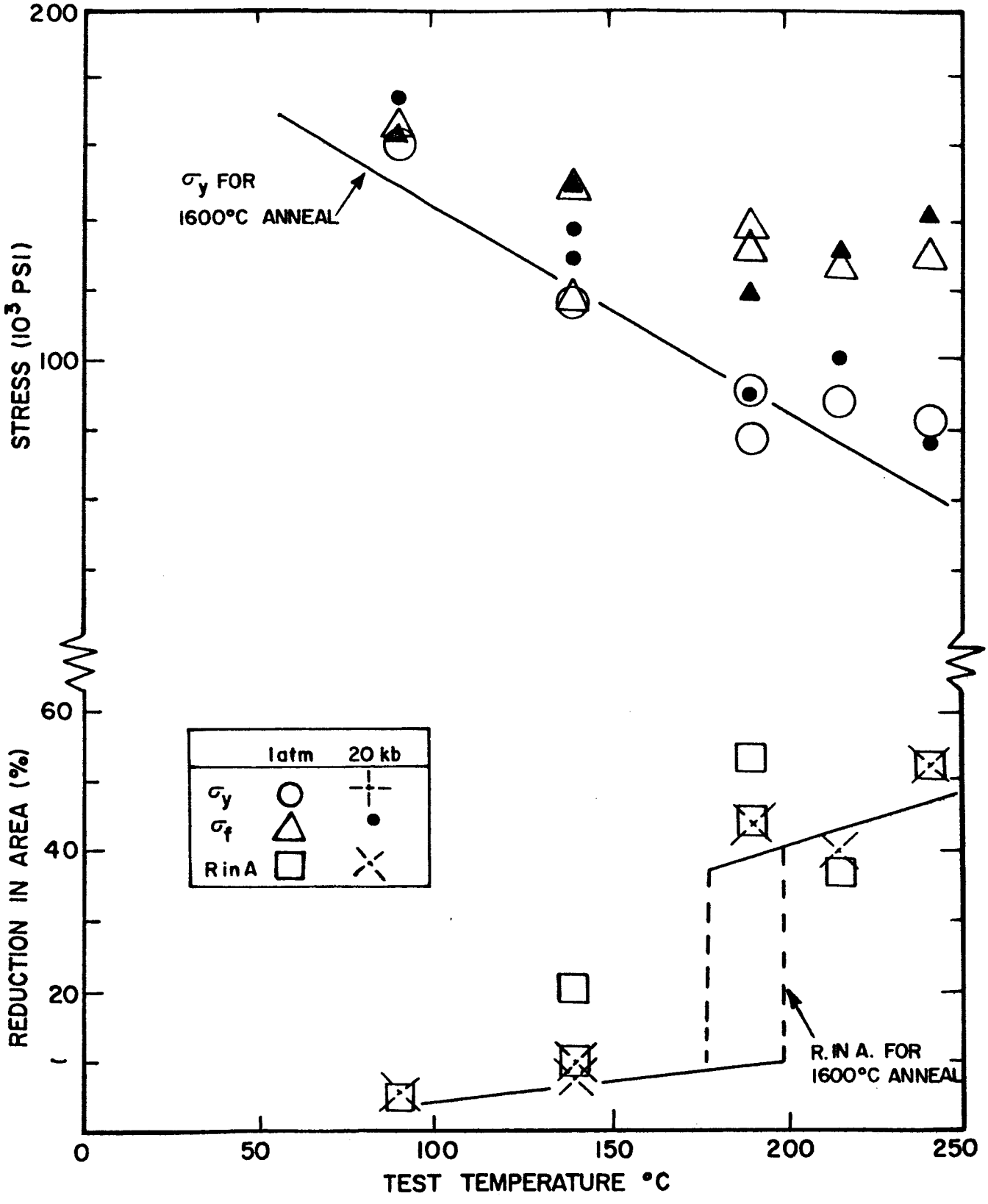


Fig. 7. Effect of test temperature on tensile properties of tungsten wire (0.030 in.diam) annealed at 2200°C: (a) as annealed; (b) after subjection to 20 kilobars. The curves compare the data with that for the 1600°C anneal.

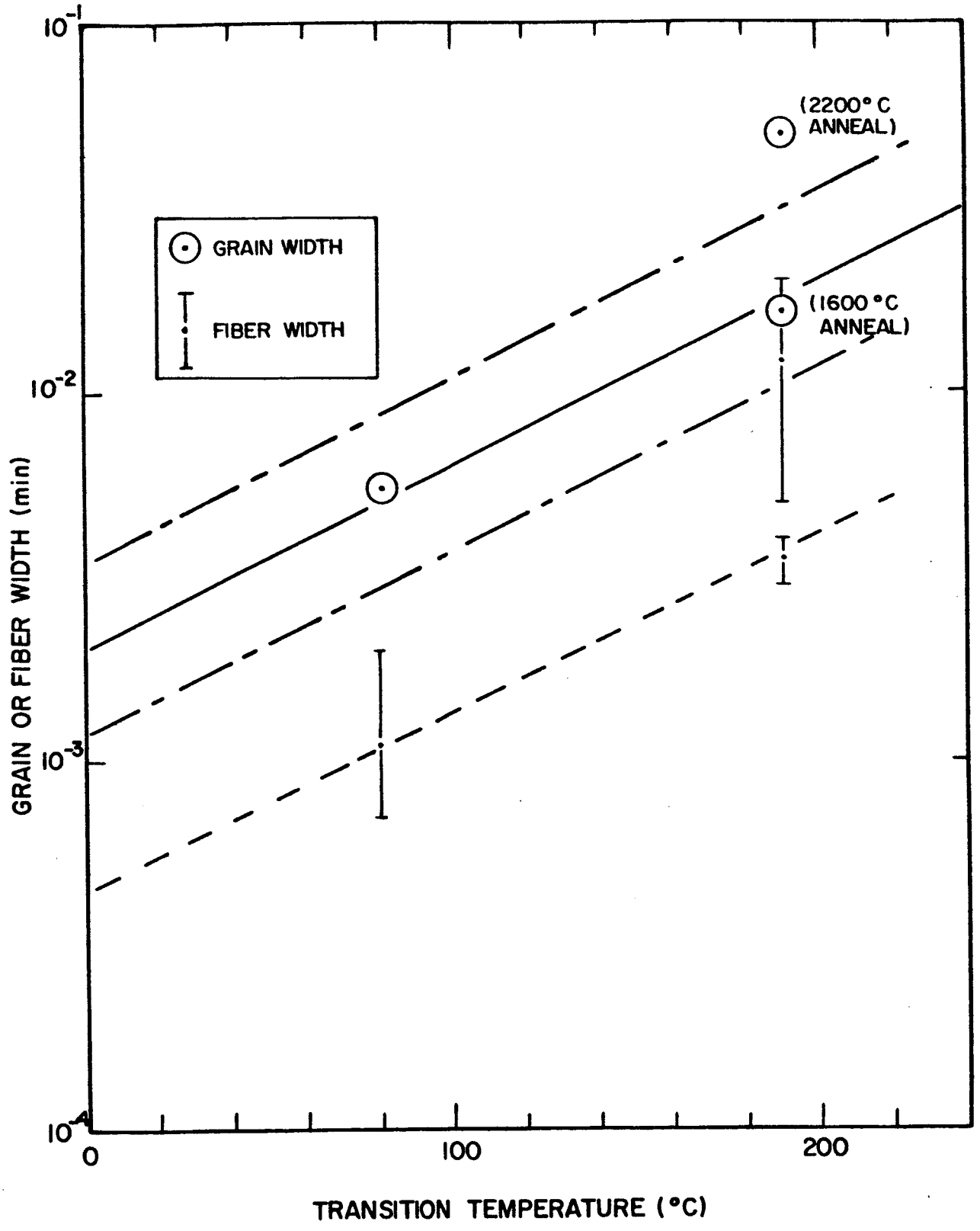


Fig. 8. Relation between grain size and ductile-brittle transition temperature for annealed tungsten wire (0.030 in. diam.).

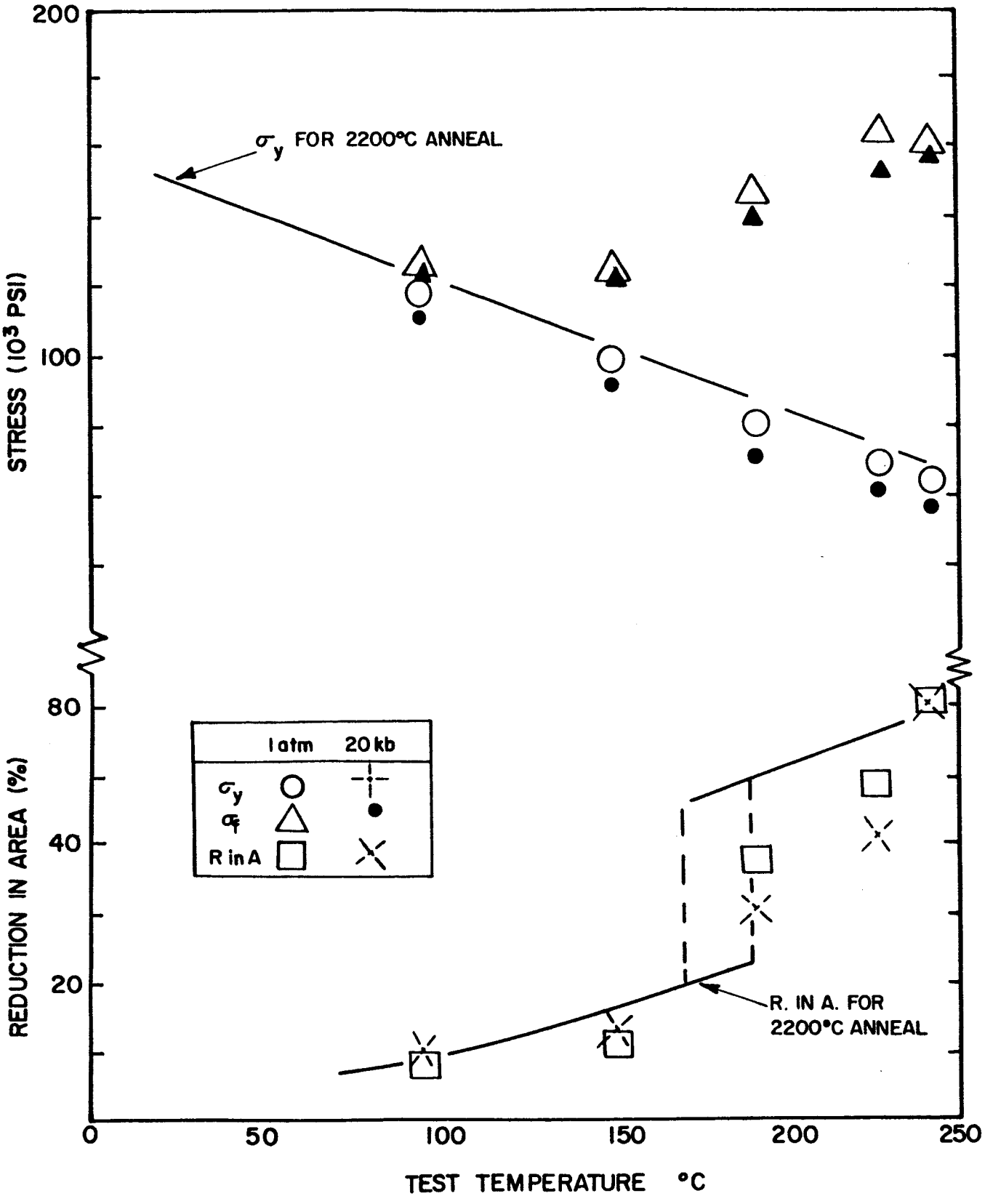
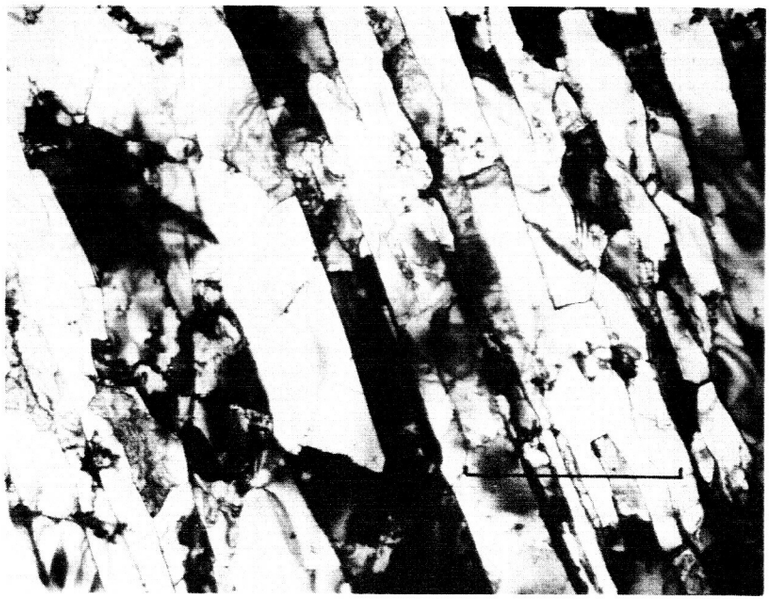


Fig. 9. Effect of test temperature on tensile properties of tungsten-1% thoria wire (0.030 in.diam) annealed at 2600°C. (a) as annealed; (b) after subject to 20 kilobars. The curves compare the data with that for the 2200°C anneal.

(a) As drawn

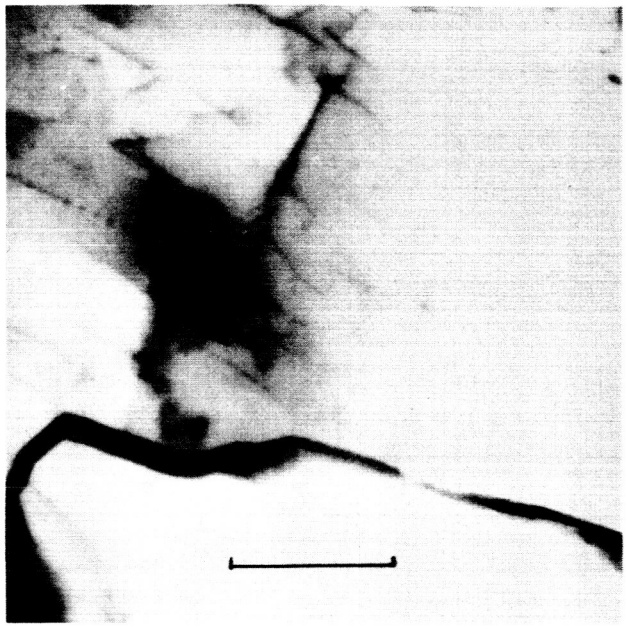
(b) 700°C



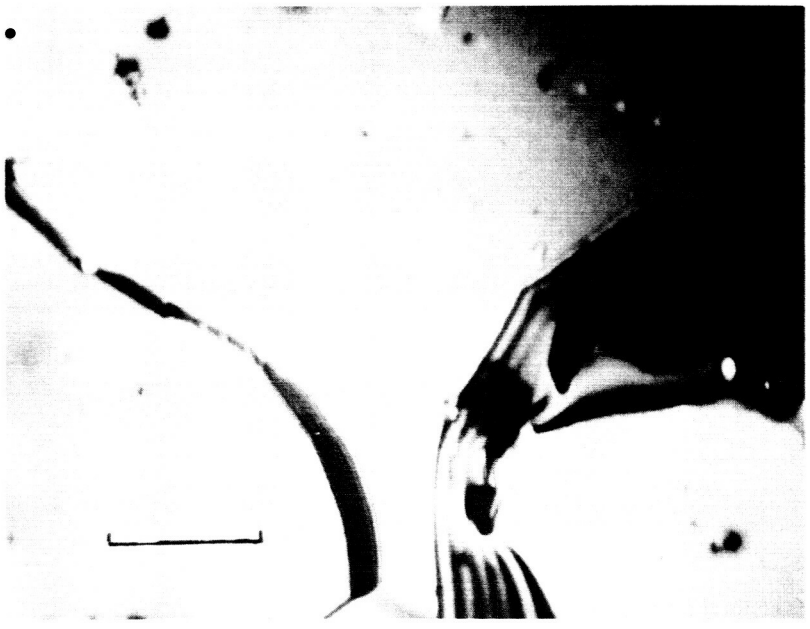
(c) 1000°C

Fig. 10 Thin foil electron micrographs of longitudinal sections of 0.030 in. diameter powder metallurgy tungsten wire illustrating changes in structure on annealing at indicated temperatures. Scale markers indicate 1 micron.

(d) 1300°C

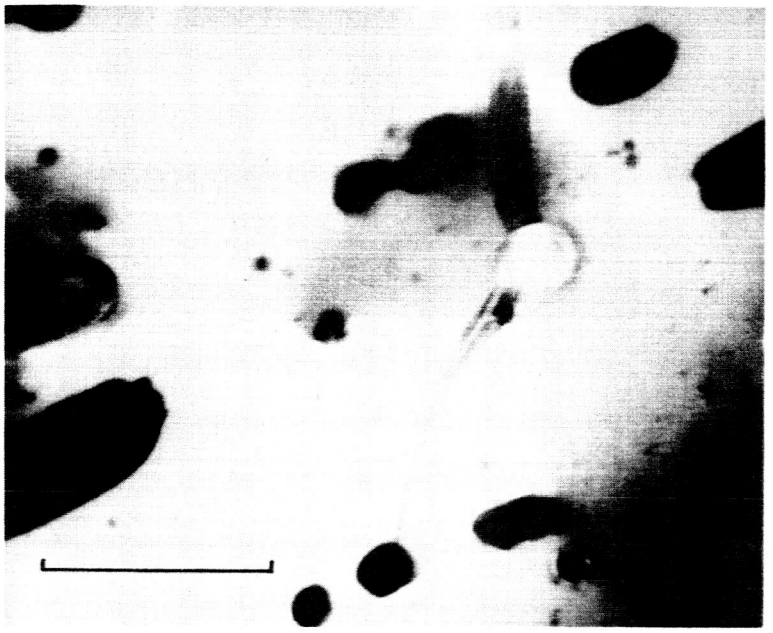


(e) 1600°C

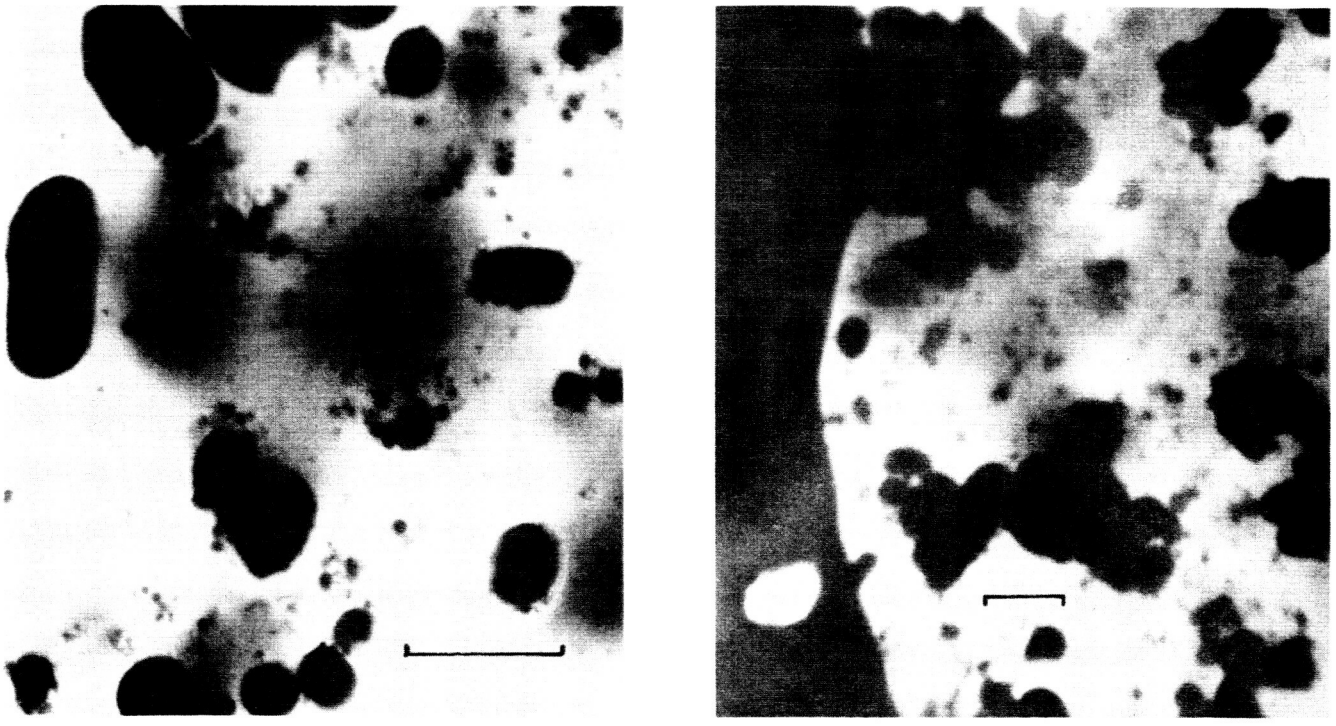


(f) 2200°C

Fig. 10 - continued



(a) 2000°C

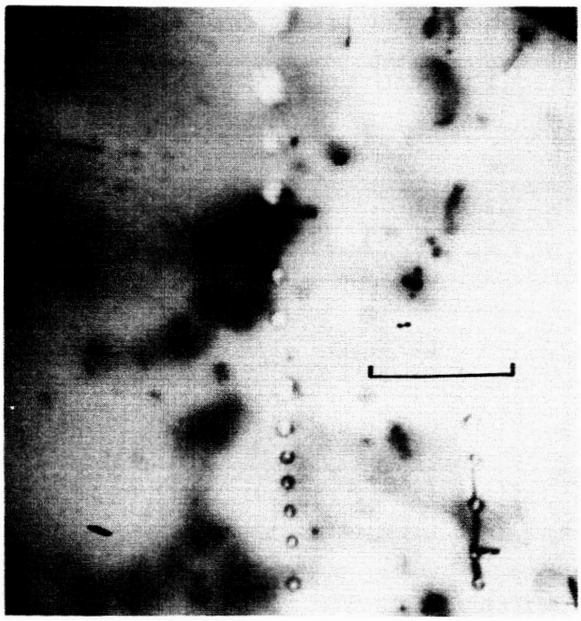


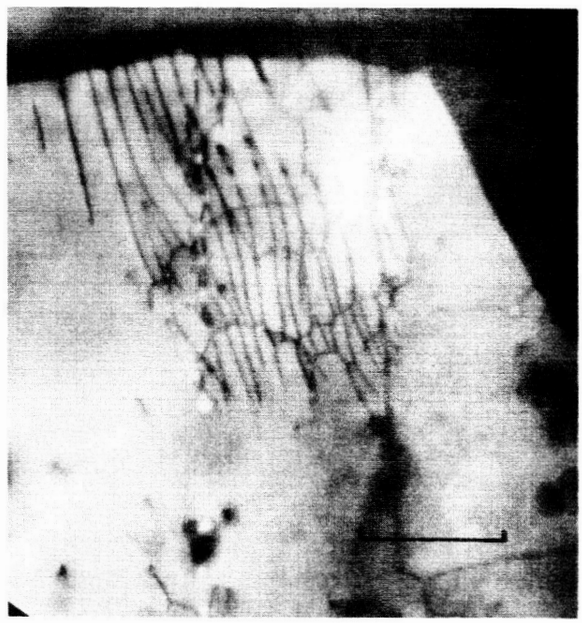
(b) 2200°C

Fig. 11. Thin foil electron micrographs of longitudinal sections of 0.030 in. diam. wires of powder metallurgy tungsten-1% thoria alloy annealed at indicated temperatures. Scale markers indicate 1 micron.

(a) As drawn

(b) 1000°C





(c) 2200°C

Fig. 12. Internal void formation in powder metallurgy tungsten wire (0.030 in. diam.) on annealing. Thin foil electron micrographs of longitudinal sections. Scale markers indicate 0.5 microns.